

Environmental Baseline of Polyaromatic Hydrocarbons (PAHs) Pollutants in Ibeju-Lekki Area of Lagos State, Nigeria

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Environmental Baseline of Polycyclic Aromatic Hydrocarbons (PAHs) Pollutants in Ibeju-Lekki Area of Lagos State, Nigeria

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Abstract

Baseline concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) as well as their spatial distributions and contamination statuses have been investigated in soils and surface waters around a newly commissioned Dangote Oil Refinery located at Ibeju Lekki, Lagos, Nigeria. This investigation has been carried out during the rainy seasons in order to establish a preoperational environmental baseline which will be used in subsequent evaluations involving impact assessments and environmental monitoring. Soil and water samples have been collected systemically at different sampling points in both the refinery environment and a control point and subsequently extracted via solvent extraction methods before being subjected to Gas Chromatography-Mass Spectrometry (GC-MS) techniques for determination of sixteen Priority PAH species according to designation by the US Environmental Protection Agency (US EPA). In addition to the application of various statistical analytical approaches such as descriptive statistics, Correlation Analysis, Hierarchical Cluster Analysis and Contamination Factor Index (CFI) and Pollution Load Index (PLI), several conclusions have emerged through this research endeavor. The presence of considerable spatial variations in concentration levels of all forms of PAHs in soils were observed. High molecular weight PAHs – specifically indeno (1,2,3-cd) pyrene, dibenz (a,h) pyrene and benzo (ghi) perylene – dominate the contaminant profiles in soils while numerous sample collection stations show increased CFI and PLI values implying possible localized anthropogenic inputs derived from combustion processes, petroleum related activity, atmospheric deposition and/or surface runoff phenomena. These instances contrast sharply against the comparatively reduced CFI/PLI readings measured at control and other less affected sites implying that these areas appear to experience near background PAH level conditions only. Water samples displayed significantly reduced concentration levels compared to those recorded in soil samples highlighting lesser persistency in the aqueous environment. Finally, there exists significant correlations amongst certain highly polluted sites which can imply similar origins of pollutants and corresponding transportation paths. It is expected that the data obtained will serve as useful environmental baselines for refinery host community as well as serving as necessary reference point for conducting further impact studies on its effects along with continuous surveillance efforts and development of efficient pollution mitigation measures for reducing consequent ecological and human health risks due to exposure to petroleum derived contaminants.

Keywords: Polycyclic aromatic hydrocarbons(PAHs): Baseline assessment; Soil contamination; Water quality; Dangote Refinery

INTRODUCTION

The rapid development of civilization, coupled with the expansion of industrial processes, has brought tremendous transformation in the quality of the environment that human beings are exposed to. The contemporary world is replete with man-made chemicals that contaminate the air, water, soil, and food chain. They are present in areas situated distant from their original points of manufacture or application. Anthropogenic processes significantly contribute a variety of chemical substances to the atmospheric environment of urban regions through activities such as production and utilization of automobiles (Matsumoto and Hanya, 1980).

Contemporary science has established the existence of over 600 organic substances in nature, the most significant of which are classified into the following categories: petroleum hydrocarbons, polycyclic aromatic hydrocarbons, ketones, aldehydes, and alcohols (Grynkiewicz et al., 2002). Volatility of organic contaminants facilitates their entrance into the air. They evaporate either from the earth's surface or from human activity emissions and are carried along with the air masses for great distances. Clouds' water become saturated with such substances and precipitation contaminates surface water and soil, often far distant from the points of emissions (Grynkiewicz et al., 2002).

Organic pollutants are broadly classified into two categories: volatile organic compounds (VOCs) and semi-volatile organic compounds, most of which also fall under the category of persistent organic pollutants (POPs). The VOC class comprises a variety of species with varying physical and chemical characteristics. One large subclass of VOCs consists of pure hydrocarbons with just carbon and hydrogen elements, including alkanes, alkenes, alkynes, and aromatic compounds. POPs, on the contrary, are chemical compounds which remain in the environment, accumulate in the food chain and also present a hazard of producing harmful effects to the environment and human health. That there is long-range transport of these chemicals to areas where they have not been used or produced, and the effects radiating from them to the entire ecosystem, justifies the imperative for ongoing monitoring to mitigate their environmental impacts (UNEP, 2009).

There is a growing concern regarding persistent organic pollutants (POPs) like PAHs. In May 2001, a global treaty for POPS regulations was signed: the 'Stockholm convention' with instruments for the total elimination of the 12 POPs worldwide (Garban et al., 2002). They carry out large-scale programs on long-range transboundary atmospheric pollution (European Monitoring and Evaluation Program, EMEP) or their emission into the sea (Oslo and Paris Convention OSPAR). PAHs are among the 12 POPs and benzo(a)pyrene (BaP) is the most toxic PAH. The aim of this convention is to manage, minimize, or prevent the release, emissions, and losses of persistent organic pollutants (POPs) into the environment (Garban et al., 2002).

Refineries are industrial plants that employ a range of chemical processes to transform crude oil into useful products. Once refined, these products then become highly valuable because of their wide range of potential

uses in other industrial processes. Whether it is plastic containers, clothes, home appliances, the detergents and medicines we use, the transport we choose or the heating in our homes, countless everyday objects and business processes require petroleum-derived substances for their operation or manufacture. As a result, oil refineries are essential for producing the raw materials we need to make both our home and work lives easier in any social or economic sphere. At the same time, these refining processes are one of the most significant contributors to air pollution (Galvan, 2007), both near the facility and further afield, and can dramatically worsen the healthy conditions of the environment not only for humans, but also for animals.

The various oil refining processes are the oil industry's principal source of air emissions. They release gases such as carbon monoxide, Sulphur dioxide, nitrogen oxides and volatile organic compounds into the air, as well as emitting high concentrations of a harmful combination of small chemicals in both a solid and liquid state, known as suspended particles or particulate matter. In 2022, the world's oil refinery capacity almost reached 102 million barrels per day. Overall, global refinery capacity has nearly doubled in the past fifty years, experiencing the largest growth during the 1970s (Adebiyi, 2002)

The refinery emissions of oil refineries are largely due to crude oil refining operations, which involve distillation, hydrotreating, and reforming. These operations emit volatile substances, like hydrocarbons, greenhouse gases (CO₂, CH₄), nitrogen oxides (NO_x), and sulphur dioxide (SO₂), along with other harmful pollutants. Some of these are even not visible to the naked eye, and therefore monitoring them becomes even more important.

Oil refinery activities from new oil refineries always involve moving large amounts of equipment into mostly rural areas for the construction of new smaller operational units. Oil- and gas-related equipment often involves heavy machinery, trucks, pipe, large warehouses, storage tanks, fluids, and parking areas to support oil refinery activities. New roads are constructed to access and service newly constructed operational units. Storage water bodies will be created to provide water to support various mechanical, chemical and industrial activities. Together, these activities could result in alterations to the soil and water compositions of the environment. The rapid expansion of infrastructure associated with oil refinery activities increases potential pathways for inorganic and organic contaminants to enter environment.

1.0.1 The New Oil Refinery – Dangote Refinery

The New Oil Refinery is located in the South-East of the Lekki Free Trade Zone (FTZ) in Ibeju-Lekki, Lagos, near the Lekki Lagoon, along the coast of Atlantic Ocean, covering a land area of approximately 2,635 hectares. It is Located on coordinates Latitude 6.45873° or 6° 27' 31" north; Longitude 4.01409 degrees or 4° 0' 51". The refinery is a 650,000 barrels per day (bpd) integrated refinery and petrochemical project which is expected to be Africa's biggest oil refinery and the world's biggest single-train facility. The refinery processes a variety of light and medium grades of crude to produce Euro-V quality clean fuels including gasoline and diesel as well as jet fuel and polypropylene. The geographical location of the refinery

is ideal for easy transshipment of the refined petroleum products to international markets. Dangote built a jetty near the project site to receive heavy equipment for the construction (<https://nseenergybusiness.com/projects/dangote-refinery-lagos>).

The New Oil Refinery has posed to be an important source of oil and natural gas in Nigeria and will contribute greatly to the energy production of the country. The refinery is a 650,000 barrels per day (bpd) integrated refinery and petrochemical project which is expected to be Africa's biggest oil refinery and the world's biggest single-train facility (<https://nseenergybusiness.com/projects/dangote-refinery-lagos>). The extensive development of oil and natural-gas resources especially with the operations of the New Oil Refinery has led to questions regarding possible environmental effects of processes associated with oil and natural-gas production, in particular to the communities housing these facilities.

Oil and natural-gas production from the New Oil Refinery involves moving large amounts of equipment into mostly rural areas for the construction of new plants. Oil- and gas-related equipment often involves heavy machinery, trucks, pipe, large warehouses, storage tanks, fluids, and parking areas to support oil and natural-gas production activities. New roads are constructed to access and service newly constructed plants and production locations. The rapid expansion of infrastructure associated with oil and natural-gas production increases potential pathways for inorganic and organic contaminants to enter surface-water systems (Kappel et al, 2013).

1.1 POLYAROMATIC HYDROCARBONS (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment, formed naturally by forest fires, volcanoes, plants, fungi and bacteria, or anthropogenically through the combustion of fuels (Albers, 2003). Generally, the presence of PAHs in the environment has increased over the last hundred years; however, global concentrations may have stabilized due to recent air and water quality regulations (Fernandez et al, 2000). PAH concentrations in the environment are often related to local and regional sources, although remote areas can be sites of PAH deposition through atmospheric processes and long range transport (Escartin et al, 1999)

Polycyclic aromatic hydrocarbons (PAHs) or poly-nuclear aromatic hydrocarbons are organic compounds that consist of two or more benzene rings joined in a linear or cluster fashion. PAHs are highly stable organic contaminants and are made up exclusively of carbon and hydrogen. They predominantly exist as complicated mixtures, not as pure compounds. PAHs tend to naturally occur, though they are also produced as pure compounds for the purpose of scientific investigation. Polycyclic aromatic hydrocarbons (PAHs) in their natural chemical forms are generally colorless, white, or pale yellow-green solids (ATSDR, 1990). The substances may possess a faint and pleasant odor (Crystal and Foster, 1991). PAHs containing up to four fused benzene rings are known as light PAHs and those containing more than four benzene rings are

called heavy PAHs. Heavy PAHs are more stable and more toxic than light ones. PAHs are lipophilic in nature; nevertheless, some of them can dissolve quite well in water (ATSDR, 1995). Of the hundreds of known PAHs, sixteen have been designated high priority pollutants by the United States Environmental Protection Agency (U.S. EPA) (Patel et al, 2020).

They have been reported to be carcinogenic, mutagenic and teratogenic in nature. Due to these natures combined with their environmental persistence, they have been included in the priority pollutants list by the United States Environmental Protection Agency (US-EPA) and the European Environment Agency (Adkonis et al., 2006). It is therefore necessary that their environmental concentrations are monitored (Charalabaki et al., 2005). Furthermore, these compounds possess high boiling and melting points along with high molecular weights, which enable their resistance to elevated temperatures generated by combustion reactions in motor and airplane engines. The majority of these compounds exhibit low water solubility (Nekhavambe, 2008). Additional detailed description of the individual polycyclic aromatic hydrocarbons (PAHs) is given below:

i) Naphthalene: Naphthalene, also referred to by the other names naphthalin, bicyclo[4.4.0]deca-1,3,5,7,9-pentene, or antinite, is characterized as a white crystalline solid with the chemical formula $C_{10}H_8$, which is a structure composed of two fused benzene rings. Naphthalene is recognized as the classic or principal component applied in mothballs. Naphthalene is a volatile substance, creating a flammable vapor and sublimating easily at room temperature, causing it to release a characteristic odor that is detectable at mass concentrations as low as 0.08 mg/Kg (Amoore et al., 1983). It has been derived from a special kind of naphtha, a generic term applied to any volatile, flammable liquid hydrocarbon mixture, such as those from coal tar. Exposure to big amounts of naphthalene can eliminate or damage red blood cells (Amoore et al., 1983).

ii) Acenaphthene: Acenaphthene, or 1,2-dihydroacenaphthylene, highlights its status as a hydrogenated acenaphthylene derivative. It is a polycyclic aromatic hydrocarbon (PAH) consisting of naphthalene bridged by an ethylene bridge at the 1,8 positions. It is also a component of coal tar and has the chemical formula $C_{10}H_{12}$ (ATSDR, 1990).

iii) Phenanthrene: Phenanthrene is a PAH consisting of three fused benzene rings and is of the formula $C_{14}H_{10}$. Phenanthrene has a name derived from phenyl and anthracene. In pure form, it occurs in cigarette smoke. It is reported as an irritant and sensitizing skin to light. It is a white powder with blue fluorescence. It is derived from fractional distillation of coal-tar oils (Wendland et al., 1963).

iv) Fluoranthene: Fluoranthene is a PAH made up of naphthalene and benzene units that are bridged by a four-membered ring. It has the molecular formula $C_{16}H_{10}$ and it is a structural isomer of the alternant PAH

pyrene. However, it is less thermodynamically stable than pyrene since its electrons cannot resonate across the whole structure like the corresponding ones in pyrene.

It is typically present in various combustion products, along with other polycyclic aromatic hydrocarbons (PAHs). It is an indicator of lower-temperature or incomplete combustion processes because non-alternant PAHs are less preferred than alternant PAHs. Fluoranthene was also isolated from coal tar pitch (FSESI, 2009).

v) Pyrene: Pyrene is a polycyclic aromatic hydrocarbon (PAH) with the molecular formula $C_{16}H_{10}$ and is made up of four benzene rings fused together, giving rise to an aromatic planar system. Pyrene exists as a colorless solid and is the smallest peri-fused PAH in which rings are fused by more than one face. Pyrene is formed as a byproduct in the incomplete combustion of organic material. Pyrene was initially isolated from coal tar, where it is present in up to 2% by weight (Senkan et al., 2003). Due to its peri-fused polycyclic aromatic hydrocarbon (PAH) ring structure, pyrene is far more resonance-stabilized than its five-membered ring isomer fluoranthene. Consequently, pyrene can be generated under a wide range of combustion conditions. For instance, automobile emissions yield approximately $1\text{ }\mu\text{g/km}$ (Senkan et al., 2003).

Although pyrene is less toxic than benzopyrene, in studies on animals it has been proved to be nephrotoxic and hepatotoxic (Senkan et al., 2003).

vi) Chrysene: Chrysene is a polycyclic aromatic hydrocarbon (PAH) of molecular formula $C_{18}H_{12}$, consisting of four fused benzene rings. It was originally isolated and described from coal tar, in which it occurs naturally. It also occurs in creosote, a chemical compound used for preserving wood. Chrysene is formed in limited amounts in coal combustion or coal, crude oil, and organic plant material distillation processes (FSESI, 2009). The derivation of the name chrysene is from Greek $\chi\rho\upsilon\varsigma\omicron\varsigma$ (chrysos), thought to be the true colour of the compound at the time of its isolation and characterization (FSESI, 2009). Pure chrysene is colorless, and the yellow coloration is due to the presence of traces of its yellow-orange isomer tetracene, which is not readily separated (FSESI, 2009).

The presence and proportions of PAHs in the environment can provide some information on the scale and amount of organic contamination. volatilization and oxidation can rapidly eliminate many common PAHs from the water column, thus PAHs generally have a short residence time in aqueous solution. consequently, the presence of PAHs in water column usually indicate recent or chronic pollution (Mastran et al, 1994). the incorporation of PAHs into underlying sediments reduces the effect of external or degrading forces and volatilization, the presence of PAHs in lake sediments can provide additional insight into deposition sources and rates (Darren et al, 2005)

The PAH composition in water and sediment can indicate the source(s) from which the PAHs were derived (Yan et al, 2004). Larger concentrations of lower molecular weight PAHs most often occur in sample

2.0.2 Study Area

The New Oil Refinery is located in the South-East of the Lekki Free Trade Zone (FTZ) in Ibeju-Lekki, Lagos, near the Lekki Lagoon, along the coast of Atlantic Ocean, covering a land area of approximately 2,635 hectares. It is Located on coordinates Latitude 6.45873° or 6° 27' 31" north; Longitude 4.01409 degrees or 4° 0' 51". Ibeju-Lekki (home of the New Oil Refinery), situated within the Lagos State town of Lekki, stands out for its exquisite charm, earning it the moniker “The New Lagos” and establishing itself as one of the most affluent neighborhoods in Lagos State. Bordered by Ogun State to the north, Eti-Osa LGA to the west, Epe LGA to the east, and the Atlantic Ocean to the south, with a population exceeding 100,000. Ibeju- Lekki is about 75km long and 20 km at its widest point and is spread over 646km² or a quarter of the total land mass of Lagos state. Located along the coastal plain of Nigeria, Ibeju-Lekki has many creeks and Lagoons and it is mainly populated by Ijebu speaking people of the Yoruba tribe in Nigeria. Indigenes of Ibeju Lekki are mainly fishermen, who traverse the length and breadth of both Lagos Lagoon and Atlantic Ocean for different species of fishes, cray fish, prawn, lobsters and crabs. The resultant effect of this is that the women smoke/grill the catches from their husbands’ nets. Smoked fish is a local delicacy which has been exported and is popularly eaten with sour garri, a local derivative of cassava, usually produced by Ijebu women. Indigenes of Ibeju Lekki also produce brooms, coconut oil and palm oil from the abundant coconut and palm trees that grow along the coastline (<https://nseenergybusiness.com/projects/dangote-refinery-lagos>).

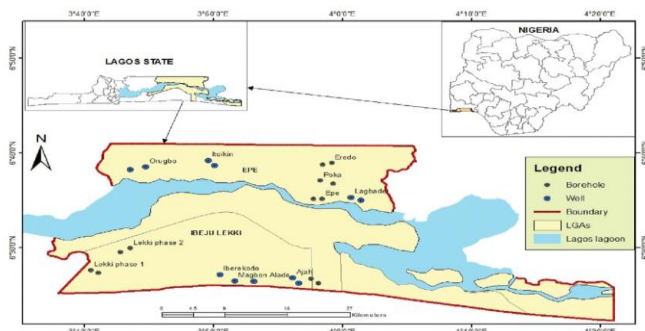


Fig. 2.2: Map Showing Study Area



Fig. 2.3: Aerial/Satellite View of the Refinery



Figure 2.4: Sunset View of the New Oil Refinery



Figure 2.5: Day View the New Oil Refiner

2.1 CHEMICALS AND REAGENTS

Analytical grade n-hexane (99%), dichloromethane (99%) and acetone (99.5%) were purchased from Thermo Fisher Scientific, Waltham, Massachusetts, USA. Activated silica gel, anhydrous sodium sulphate and deionized water were obtained from Sigma-Aldrich, St. Louis, Missouri, USA. Trioxonitrate (IV) acid and hydrochloric acid were supplied by Thermo Fisher Scientific, Waltham, Massachusetts, USA. All chemicals and reagents used throughout the research were of analytical grade.

2.2 SAMPLE COLLECTION

Water for the study were sampled according to the method of S. T. Grassloff, 1983. Water samples were collected directly from sample source using a properly pre-cleaned amber bottles. The bottles were first rinsed with the sample water before collection and collected samples were stored in ice-packed cooler and thereafter transported to the laboratory refrigerator for storage at temperature of 4°C until time for analysis. pH of water samples was determined and recorded at the point of collection. Soil samples were collected using soil auger, stored in sealable polythene zipper bags and kept in ice-packed cooler, thereafter transported to the laboratory refrigerator for storage at 4°C temperature until time of analysis. All collected samples were appropriately labeled. GPS location/coordinates of sample collection points were also taken and recorded. Analysis of the samples were carried out within 24 hours of sample collection.

2.2.1 Sample Preparation – Soil Sample

Apparatus used were Sieve, Analytical balance, Ultrasonic bath, Filter paper, Rotary evaporator, Beakers, Measuring cylinders and Spatula

2.2.3 Procedural Steps

- i. Air dried soil samples were sieved to obtain a uniform particle size
- ii. 5 g of soil sample was weighed into a glass beaker
- iii. 50 ml solvent hexane:acetone (1:1) was added to the sample in an ultrasonic bath and sonicated for 20 minutes at 30°C
- iv. After the first extract, the beakers were swirled and sonication was repeated. This was done 3 to 4 times to ensure maximum recovery/extraction
- v. The extracts were combined, filtered and passed through activated silica gel and anhydrous sodium sulphate for clean-up
- vi. After clean-up, extract was concentrated using rotary evaporator at low temperature
- vii. Sample was then taken for GC-MS analysis (Andrianova & Quimby, 2019)

2.2.4 Sample Preparation – Water Sample

Apparatus used were Retort stand, Separatory funnel, Measuring cylinder, beakers, flasks, Funnel and Rotary evaporator

2.2.5 Procedural Steps

- i. 50 ml water sample was measured into the separatory funnel
- ii. 5 ml dichloromethane was added into the sample in the separatory funnel as the solvent of extraction
- iii. The mixture was then shaken vigorously several times to allow the analytes to partition between the two liquid phases
- iv. After allowing the phases to separate, the extract was collected
- v. The extraction was repeated multiple times to ensure efficient recovery of the analytes
- vi. The extracts were then added together and passed through anhydrous sodium sulphate for clean-up
- vii. Afterwards, the volume was reduced using rotary evaporator (Anderson et al, 2015)

2.3 PREPARATION OF STANDARDS

PAH standard, 2000 mg/Kg (Catalog Number Z-014) containing 16 PAHs components purchased from AccuStandard by Lagos State Environmental Protection Agency (LASEPA) were acquired and used to prepare a 5-point dilution calibration standards (0.1mg/Kg, 0.05mg/Kg, 0.025mg/Kg, 0.06mg/Kg and 0.03 mg/Kg). A stock standard solution of the PAHs was prepared by dissolving 5 ml of the reference standard (2000mg/Kg) in 100 ml of deionized water to make 100 ml stock solution from which the calibration standards were prepared using serial dilution. 20 µL of each working standard (in duplicates) was spiked into the GC-MS; the retention time and respective peak areas were created. The peak of the analyte was found by comparing the retention time of the ratio of analyte in the sample to that of the standard. (The calculations are contained at the index).

2.4 METHOD VALIDATION

Recovery Studies

20 µL of 0.1 mg/Kg mixed standard was added to 5g of sample and analysis was carried out. Percentage recovery was determined according to the following equation (Harris, 2001):

$$\% \text{ Recovery} = \frac{\text{Conc. of spiked Sample} - \text{Conc. of unspiked sample}}{\text{Concentration of added standard}} \times 100$$

Calibration Curves

The calibration plot of the heavy metals was achieved by plotting mean peak areas derived from replicate analysis of their standard solutions versus their respective concentrations.

The limit of detection (LOD) and limit of quantification (LOQ) are calculated using the equations below;

$$\text{LOD} = \frac{3 \times \text{standard deviation}}{\text{slope of calibration curve}}$$

$$\text{LOQ} = \frac{10 \times \text{standard deviation}}{\text{slope of calibration curve}}$$

2.5 INSTRUMENT DESCRIPTION

An Agilent 7890B GC with an Agilent 5977B MSD System equipped with a split/splitless inlet and an Agilent 7693 Automatic Liquid Sampler was used for this analysis. Analysis was run in duplicate. The table below shows the instrumental conditions used in the data acquisition.

Table 2.1: Chromatographic Conditions

GC	Agilent 7890B coupled with 5977B Mass selective Detector
Sampler	Agilent 7693 Injector tower with 10µL syringe
Carrier	Helium [flow; 1.2mL/min]
Injection	1µL Splitless, 250 °C
Column	HP-5ms Ultra Inert 30 m, 250 µm, 0.25 µm
Oven	50 °C (hold 1 min) to 270 °C at 20 °C/min (hold 6 min)
MSD	Transfer line temp [280] Quadrupole temp [150 °C] Ion source temp [230 °C]

RESULTS AND DISCUSSION

Table 3.1: PAH Concentration in Soil Sample

PAH	UNIT	CSWE 1B	SWS 2A	CSWE 2B	SS 9A	SS 10B	SS 13B	SS 14B	SS 15A	SS 16B	SW 5A	SWS 3B	SS 15A
Naphthalene	mg/Kg	0.20	0.03	0.08	0.10	0.02	0.17	0.02	0.25	0.07	0.03	0.04	0.19
Acenaphthylene	mg/Kg	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08
Acenaphthene	mg/Kg	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.08
Fluorene	mg/Kg	0.00	0.00	0.00	0.01	0.00	0.01	0.03	0.01	0.01	0.01	0.01	0.08
Phenanthrene	mg/Kg	0.01	0.00	0.00	0.00	0.00	0.00	0.05	0.03	0.00	0.01	0.00	0.13

Anthracene	mg/Kg	0.01	0.04	0.00	0.04	0.00	0.01	0.02	0.03	0.00	0.01	0.01	0.14
Fluoranthene	mg/Kg	0.04	0.00	0.05	0.42	0.00	0.08	0.13	0.40	0.02	0.02	0.02	0.21
Anthracene	mg/Kg	0.01	0.00	0.09	0.06	0.01	0.02	0.20	0.06	0.00	0.00	0.00	0.3
Pyrene	mg/Kg	0.10	0.04	0.03	0.10	0.02	0.07	0.07	0.24	0.07	0.02	0.02	0.3
Benz(a)anthracene	mg/Kg	0.11	0.05	0.05	0.46	0.08	0.07	0.13	0.27	0.06	0.02	0.03	0.34
Chrysene	mg/Kg	0.06	0.03	0.01	0.12	0.03	0.03	0.03	0.07	0.02	0.00	0.00	0.03
Benzo(b)fluoranthene/benzo(k)													
Fluoranthene	mg/Kg	0.83	0.16	0.09	3.46	0.25	0.20	0.09	0.62	0.16	0.00	0.00	1.04
Benzo(a)pyrene	mg/Kg	0.70	0.15	0.61	0.07	0.28	0.25	0.03	0.94	0.24	0.00	0.04	0.68
Indeno(1,2,3-cd)pyrene/Dibenz(a,h)pyrene													
Indeno(1,2,3-cd)pyrene/Dibenz(a,h)pyrene	mg/Kg	15.20	0.93	1.64	0.25	9.65	2.51	14.72	9.92	1.42	0.01	0.07	0.19
Benzo(ghi)perylene	mg/Kg	1.72	0.49	6.26	5.38	6.33	3.21	7.73	9.01	2.67	0.03	0.31	0.08

Table 3.2: Descriptive Statistics of PAH concentrations in Soil Samples

	Minimum	Maximum	Mean		Std. Deviation
	Statistic	Statistic	Statistic	Std. Error	Statistic
SS 9A	0.02	19.31	3.2541	1.53227	5.52466
SS 10B	0.00	7.23	0.8679	0.55450	1.99927
SS 13B	0.00	13.30	1.3452	1.01955	3.67605
SS 14A	0.00	1.07	0.1012	0.08189	0.29527
SS 15A	0.00	1.40	0.3510	0.14199	0.51195
SS 16B	0.00	3.38	0.7301	0.31493	1.13551
SW 5A	0.00	1.66	0.3902	0.16132	0.58165
SW 52A	0.00	9.38	1.7527	0.77388	2.79025
SWS 3B	0.00	2.33	0.3682	0.20225	0.72921
SS 15A	0.01	0.70	0.2200	0.05732	0.20668

3.0.1 Descriptive Statistics

The mean PAH concentration increases in the order as SW 5A (0.01) < SWS 3B (0.016) < SWS 2A (0.154) < SS 16B (0.225) < SS 13B (0.361) < SS 9A (0.653) < SS 15A (1.293) < SS 10B (1.309) < SS 14B (1.419). This clearly shows that SS 14B, SS 10B, and SS 15A have the highest mean concentrations, while SW 5A and SWS 3B (likely control or less impacted sites) have lowest values.

Also, the High standard deviation values in SS 14B (3.802), SS 10B (2.997), and SS 15A (2.882) indicate high variability which suggests an irregular contamination inputs (e.g., runoff, industrial effluents, or oil leaks). Conversely, the low variability in SWS 3B and SW 5A indicates consistent low PAH levels, possibly background or natural.

The sites with high means and high variability (SS 14B, SS 10B, SS 15A) likely experience episodic contamination, such as oil spillage, combustion emissions, or industrial discharge while the sites with low means and low deviations (SWS 2A, SW 5A, SWS 3B) represent less impacted or reference sites, possibly distant from pollution sources.

3.0.2 Correlation Analysis

The Pearson correlation coefficients (both 2-tailed and 1-tailed) show the degree of linear relationship between sampling sites, i.e., how PAH levels in one site rise or fall in tandem with another.

The following are observed in the 2-tailed significance for a very Strong Correlations ($r > 0.8$, $p < 0.01$). As for SWS 2A ↔ SS 10B $r = 0.855^{**}$, SWS 2A ↔ SS 14B ($r = 0.866^{**}$, SS 10B ↔ SS 13B $r = 0.992^{**}$, SS 10B ↔ SS 14B $r = 0.992^{**}$, SS 10B ↔ SS 15A $r = 0.972^{**}$, SS 15A ↔ SS 16B $r = 0.965^{**}$). The Moderate Correlations ($r = 0.5-0.7$) are observed for SS 9A ↔ SS 15A $r = 0.587^{*}$, SS 9A ↔ SS 16B $r = 0.732^{**}$, SS 13B ↔ SWS 3B $r = 0.594^{*}$.

A Weak or Insignificant Correlations ($r < 0.3$, $p > 0.05$) was observed for SW 5A ↔ most sites show low correlation, confirming it as a control/isolated site.

These strong positive correlations among SS 10B, SS 13B, SS 14B, SS 15A, and SS 16B imply these sites likely share common pollution sources and are possibly industrial effluents, oil residues, or combustion-related PAHs. Moderate correlation between SWS 2A and downstream sites suggests transport or dispersion of PAHs through water flow. SW 5A and SWS 3B have low or negative correlations, confirming low anthropogenic impact or isolated hydrological pathways.

Table 3.3 Correlation Matrix (2-Tailed) of PAH Concentrations in Soil Sample

								SW	SWS		
		SS 9A	SS 10B	SS 13B	SS 14A	SS 15A	SS 16B	SW 5A	52A	3B	SS 15A
SS 9A	Pearson Correlation	1	-0.009	-0.117	-0.148	.677*	0.133	-0.156	0.104	0.011	-0.053
	Sig. (2-tailed)		0.976	0.703	0.631	0.011	0.664	0.611	0.736	0.971	0.863
	N	13	13	13	13	13	13	13	13	13	13
SS 10B	Pearson Correlation	-0.009	1	0.370	0.316	-0.060	.646*	0.260	.603*	.927**	.706**
	Sig. (2-tailed)	0.976		0.214	0.293	0.845	0.017	0.391	0.029	0.000	0.007
	N	13	13	13	13	13	13	13	13	13	13
SS 13B	Pearson Correlation	-0.117	0.370	1	.998**	-0.001	0.422	.597*	.908**	.677*	-0.016
	Sig. (2-tailed)	0.703	0.214		0.000	0.997	0.151	0.031	0.000	0.011	0.959
	N	13	13	13	13	13	13	13	13	13	13
SS 14A	Pearson Correlation	-0.148	0.316	.998**	1	-0.025	0.401	.612*	.883**	.630*	-0.055
	Sig. (2-tailed)	0.631	0.293	0.000		0.936	0.174	0.026	0.000	0.021	0.859
	N	13	13	13	13	13	13	13	13	13	13
SS 15A	Pearson Correlation	.677*	-0.060	-0.001	-0.025	1	-0.038	-0.187	0.072	0.018	-0.158
	Sig. (2-tailed)	0.011	0.845	0.997	0.936		0.903	0.541	0.815	0.952	0.605
	N	13	13	13	13	13	13	13	13	13	13

SS 16B	Pearson Correlation	0.133	.646*	0.422	0.401	-0.038	1	0.429	.559*	.627*	.641*
	Sig. (2-tailed)	0.664	0.017	0.151	0.174	0.903		0.144	0.047	0.022	0.018
	N	13	13	13	13	13	13	13	13	13	13
SW 5A	Pearson Correlation	-0.156	0.260	.597*	.612*	-0.187	0.429	1	0.493	0.407	-0.061
	Sig. (2-tailed)	0.611	0.391	0.031	0.026	0.541	0.144		0.087	0.168	0.843
	N	13	13	13	13	13	13	13	13	13	13
SW 52A	Pearson Correlation	0.104	.603*	.908**	.883**	0.072	.559*	0.493	1	.836**	0.218
	Sig. (2-tailed)	0.736	0.029	0.000	0.000	0.815	0.047	0.087		0.000	0.474
	N	13	13	13	13	13	13	13	13	13	13
SWS 3B	Pearson Correlation	0.011	.927**	.677*	.630*	0.018	.627*	0.407	.836**	1	0.511
	Sig. (2-tailed)	0.971	0.000	0.011	0.021	0.952	0.022	0.168	0.000		0.074
	N	13	13	13	13	13	13	13	13	13	13
SS 15A	Pearson Correlation	-0.053	.706**	-0.016	-0.055	-0.158	.641*	-0.061	0.218	0.511	1
	Sig. (2-tailed)	0.863	0.007	0.959	0.859	0.605	0.018	0.843	0.474	0.074	

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 3.4: Correlation Matrix (1-Tailed) of PAH Concentration in Soil Sample

		SS 9A	SS 10B	SS 13B	SS 14A	SS 15A	SS 16B	SW 5A	SW 52A	SWS 3B	SS 15A
SS 9A	Pearson Correlation	1	-0.009	-0.117	-0.148	.677**	0.133	-0.156	0.104	0.011	-0.053
	Sig. (1-tailed)		0.488	0.351	0.315	0.005	0.332	0.306	0.368	0.486	0.432
	N	13	13	13	13	13	13	13	13	13	13
SS 10B	Pearson Correlation	-0.009	1	0.370	0.316	-0.060	.646**	0.260	.603*	.927**	.706**
	Sig. (1-tailed)	0.488		0.107	0.146	0.422	0.009	0.196	0.015	0.000	0.003
	N	13	13	13	13	13	13	13	13	13	13
SS 13B	Pearson Correlation	-0.117	0.370	1	.998**	-0.001	0.422	.597*	.908**	.677**	-0.016
	Sig. (1-tailed)	0.351	0.107		0.000	0.498	0.076	0.016	0.000	0.006	0.479
	N	13	13	13	13	13	13	13	13	13	13
SS 14A	Pearson Correlation	-0.148	0.316	.998**	1	-0.025	0.401	.612*	.883**	.630*	-0.055
	Sig. (1-tailed)	0.315	0.146	0.000		0.468	0.087	0.013	0.000	0.010	0.429
	N	13	13	13	13	13	13	13	13	13	13
SS 15A	Pearson Correlation	.677**	-0.060	-0.001	-0.025	1	-0.038	-0.187	0.072	0.018	-0.158

SS 16B	Sig. (1-tailed)	0.005	0.422	0.498	0.468		0.451	0.271	0.408	0.476	0.303
	N	13	13	13	13	13	13	13	13	13	13
	Pearson Correlation	0.133	.646**	0.422	0.401	-0.038	1	0.429	.559*	.627*	.641**
SW 5A	Sig. (1-tailed)	0.332	0.009	0.076	0.087	0.451		0.072	0.023	0.011	0.009
	N	13	13	13	13	13	13	13	13	13	13
	Pearson Correlation	-0.156	0.260	.597*	.612*	-0.187	0.429	1	.493*	0.407	-0.061
SW 52A	Sig. (1-tailed)	0.306	0.196	0.016	0.013	0.271	0.072		0.043	0.084	0.421
	N	13	13	13	13	13	13	13	13	13	13
	Pearson Correlation	0.104	.603*	.908**	.883**	0.072	.559*	.493*	1	.836**	0.218
SWS 3B	Sig. (1-tailed)	0.368	0.015	0.000	0.000	0.408	0.023	0.043		0.000	0.237
	N	13	13	13	13	13	13	13	13	13	13
	Pearson Correlation	0.011	.927**	.677**	.630*	0.018	.627*	0.407	.836**	1	.511*
SS 15A	Sig. (1-tailed)	0.486	0.000	0.006	0.010	0.476	0.011	0.084	0.000		0.037
	N	13	13	13	13	13	13	13	13	13	13
	Pearson Correlation	-0.053	.706**	-0.016	-0.055	-0.158	.641**	-0.061	0.218	.511*	1

Sig. (1-tailed)	0.432	0.003	0.479	0.429	0.303	0.009	0.421	0.237	0.037
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** . Correlation is significant at the 0.01 level (1-tailed).

* . Correlation is significant at the 0.05 level (1-tailed).

3.0.3 Proximity (Dissimilarity) Matrix

The Proximity Matrix (Squared Euclidean Distance) quantifies differences in PAH concentration profiles between sites. The smaller distances mean sites are similar; larger distances mean different contamination patterns. The Smallest Distances (Most Similar) include Site 2 and 3 (0.001), Site 1 and 9 (0.019) and Site 2 and 11 (0.021). These sites have nearly identical PAH profiles.

The Largest Distances (Most Dissimilar) are seen for Sites 14 and 15 (74.598), Sites 14 and 1 (335.627), Sites 15 and 1 (187.042). This Indicates that SS 14B and SS 15A differ greatly from cleaner or low-concentration sites (like SWS 2A). The proximity results align with descriptive stats of SS 14B and SS 15A are most heavily contaminated and distinct, while SWS 2A, SWS 3B, and SW 5A form a low-contamination cluster.

Table 3.5: Proximity Matrix of Soil Sample Sites

Case	Squared Euclidean Distance												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1	0.000	0.652	103.3	380.97	5.011	9.338	2.639	0.098	0.339	4.440	278.0	111.0	17.3
			92	2							09	58	02
2	0.652	0.000	88.15	351.25	3.341	5.443	1.120	0.690	0.960	4.152	272.3	103.7	14.5
			8	0							61	59	23
3	103.39	88.158	0.000	90.041	77.87	51.48	80.59	101.8	104.6	102.1	348.7	137.0	82.6
	2				2	6	3	61	27	99	69	47	47
4	380.97	351.25	90.04	0.000	327.6	273.0	338.0	377.8	381.3	368.4	564.6	325.3	318.
	2	0	1		03	58	80	99	61	47	67	55	805
5	5.011	3.341	77.87	327.60	0.000	4.695	3.918	4.875	5.610	8.950	275.5	104.2	14.4
			2	3							26	48	21

6	9.338	5.443	51.48	273.05	4.695	0.000	5.283	8.956	10.23	13.17	284.2	100.9	15.9
			6	8					9	8	13	28	13
7	2.639	1.120	80.59	338.08	3.918	5.283	0.000	2.519	3.043	6.360	272.1	100.1	14.5
			3	0							09	37	57
8	0.098	0.690	101.8	377.89	4.875	8.956	2.519	0.000	0.350	4.536	277.8	110.4	16.8
			61	9							67	18	78
9	0.339	0.960	104.6	381.36	5.610	10.23	3.043	0.350	0.000	2.493	268.5	105.7	16.8
			27	1		9					52	88	06
10	4.440	4.152	102.1	368.44	8.950	13.17	6.360	4.536	2.493	0.000	243.0	92.09	17.3
			99	7		8					56	5	67
11	278.00	272.36	348.7	564.66	275.5	284.2	272.1	277.8	268.5	243.0	0.000	162.2	245.
	9	1	69	7	26	13	09	67	52	56		22	498
12	111.05	103.75	137.0	325.35	104.2	100.9	100.1	110.4	105.7	92.09	162.2	0.000	70.5
	8	9	47	5	48	28	37	18	88	5	22		78
13	17.302	14.523	82.64	318.80	14.42	15.91	14.55	16.87	16.80	17.36	245.4	70.57	0.00
			7	5	1	3	7	8	6	7	98	8	0

3.0.4 Agglomeration Schedule (Hierarchical Cluster Analysis)

This shows how sampling sites group together based on PAH similarity, merging clusters step-by-step as similarity decreases.

Stage 1 – 4 for Clusters 1,2,3,8,9,11 merge quickly (coeff < 0.1) which indicates a highly similar low-PAH sites. Stages 5 – 8 Cluster 1 sequentially merges with 7,10,13 Moderately contaminated cluster forms. Stage 9 Cluster 1 merges with 12 (coeff = 10.226) a major grouping of medium-PAH sites. The stages 10 Clusters 14 and 15 merge (coeff = 74.598) shows a high-PAH “polluted” cluster and stage 11 the final merge (coeff = 258.206) shows that all sites form one large cluster

Cluster A (Low PAH) – SWS 2A, SW 5A, SWS 3B, and possibly SS 9A (low values, high similarity).

Cluster B (High PAH) – SS 10B, SS 13B, SS 14B, SS 15A, SS 16B (high means, strong inter-correlation). The above classification supports the correlation and descriptive findings which may be due to geographically or hydrologically, pollution spreads among SS 10B - 16B while SWS sites remain relatively clean.

Table 3.6: Agglomeration Schedule of Soil Sample Sites

Stage	Cluster Combined			Stage Cluster First Appears		Next Stage
	Cluster 1	Cluster 2	Coefficients	Cluster 1	Cluster 2	
1	2	3	0.001	0	0	2
2	2	11	0.019	1	0	4
3	1	9	0.019	0	0	5
4	2	8	0.040	2	0	5
5	1	2	0.067	3	4	6
6	1	7	0.162	5	0	7
7	1	10	0.483	6	0	8
8	1	13	0.894	7	0	9
9	1	12	10.226	8	0	11
10	14	15	74.598	0	0	11
11	1	14	258.206	9	10	0

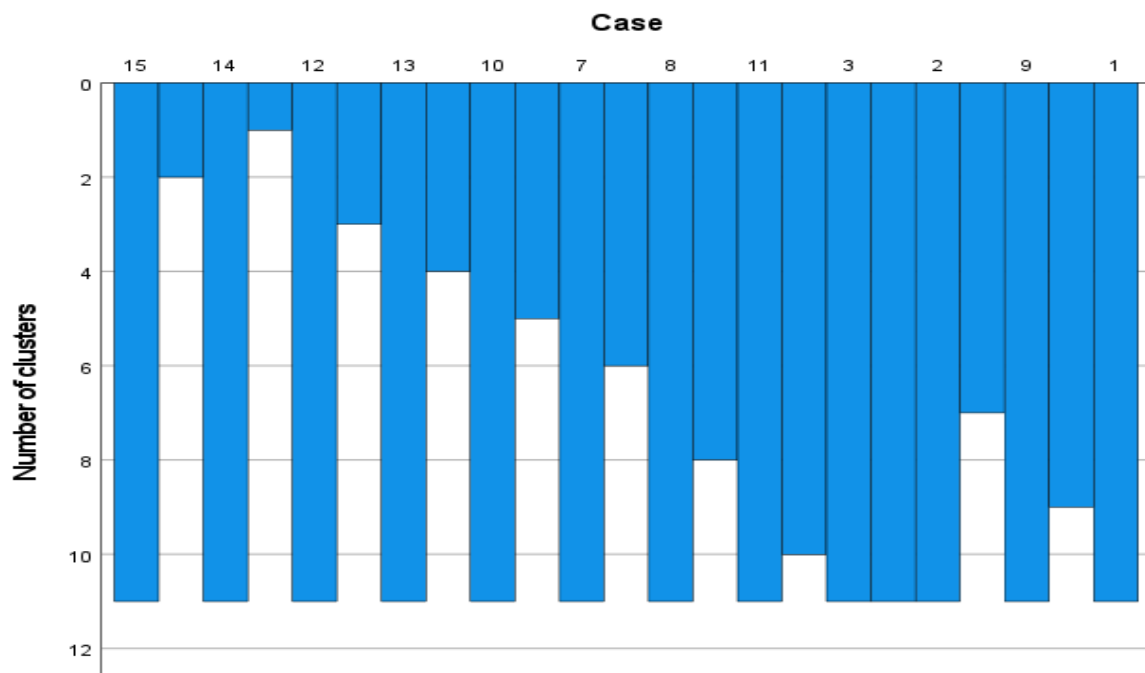


Fig. 3.1: Hierarchical Clustering of Soil Sample Sites

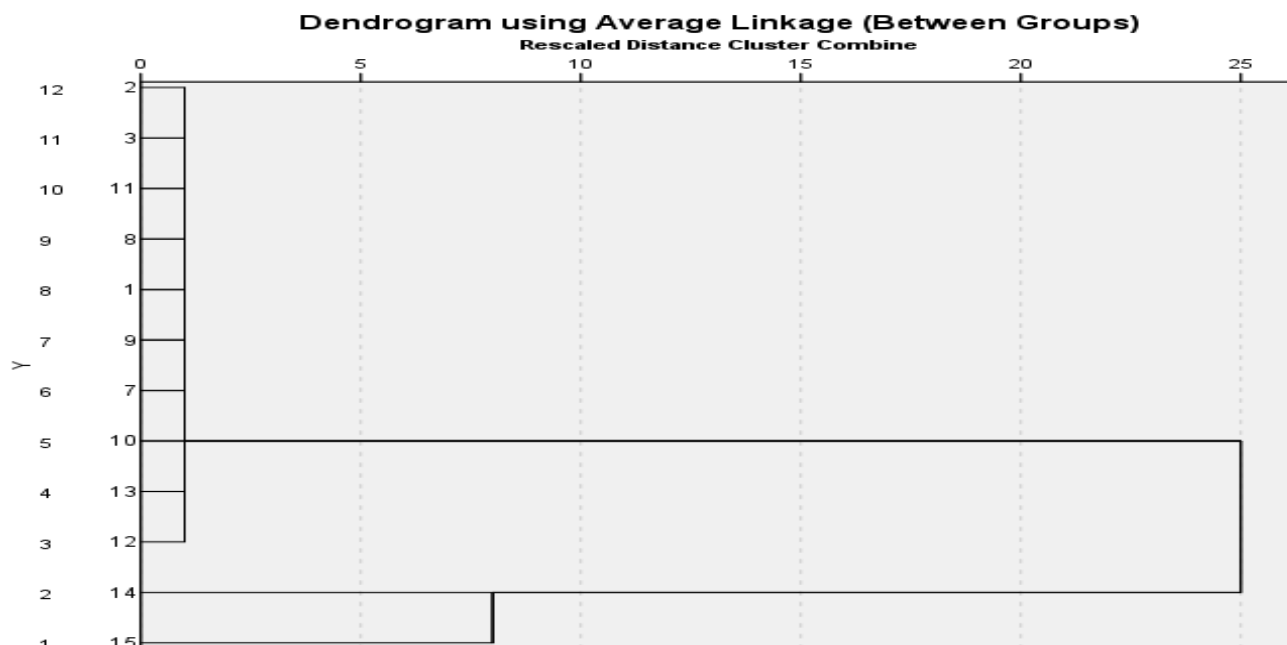


Fig. 3.2: Hierarchical Clustering Dendrogram of Soil Sample Sites

3.1 POLLUTION LOAD INDEX (PLI) AND CONTAMINATION FACTOR INDEX (CFI) FOR SOIL SAMPLE PAH RESULTS

The table below presents the derived background (Normal Background Concentration, NBC) values for seven (7) genotoxic PAHs used in the Contamination Factor Index (CFI) and Pollution Load Index (PLI) calculations. The values are shown for both the Principal domain NBCs (BaP = 0.500 mg/kg) and the Urban NBCs (BaP = 0.536 mg/kg).

Table 3.7. Derived NBC values for seven genotoxic PAHs

Compound (used in index)	Ratio to BaP	Principal (mg/kg)	NBC	Urban NBC (mg/kg)
Benzo[a]pyrene (BaP)	1.00	0.500		0.536
Benzo[a]anthracene (BaA)	1.03	0.515		0.552
Chrysene (Chr)	1.15	0.575		0.616
Benzo[b]/Benzo[k]fluoranthene (BbF/BkF)	1.12	0.560		0.600
Indeno(1,2,3-cd)pyrene (IND)	0.53	0.265		0.284

Dibenz[a,h]pyrene (DBahP)	0.37	0.185	0.198
Benzo[ghi]perylene (BghiP)	0.70	0.350	0.375

Notes: The Principal NBCs are anchored on BaP = 0.500 mg/kg (Defra/BGS principal-domain dataset) while the Urban NBCs are anchored on BaP = 0.536 mg/kg (Defra TGS BaP urban domain mean). Other PAHs were derived using literature-based BaP-to-PAH ratios commonly used in UK contaminated land guidance. The combined IND/DBahP row in earlier analysis was represented by the IND ratio (0.53). Here, they are separated for clarity. These NBCs serve as proxy values for environmental baseline comparisons when explicit per-compound NBCs are not published by Defra.

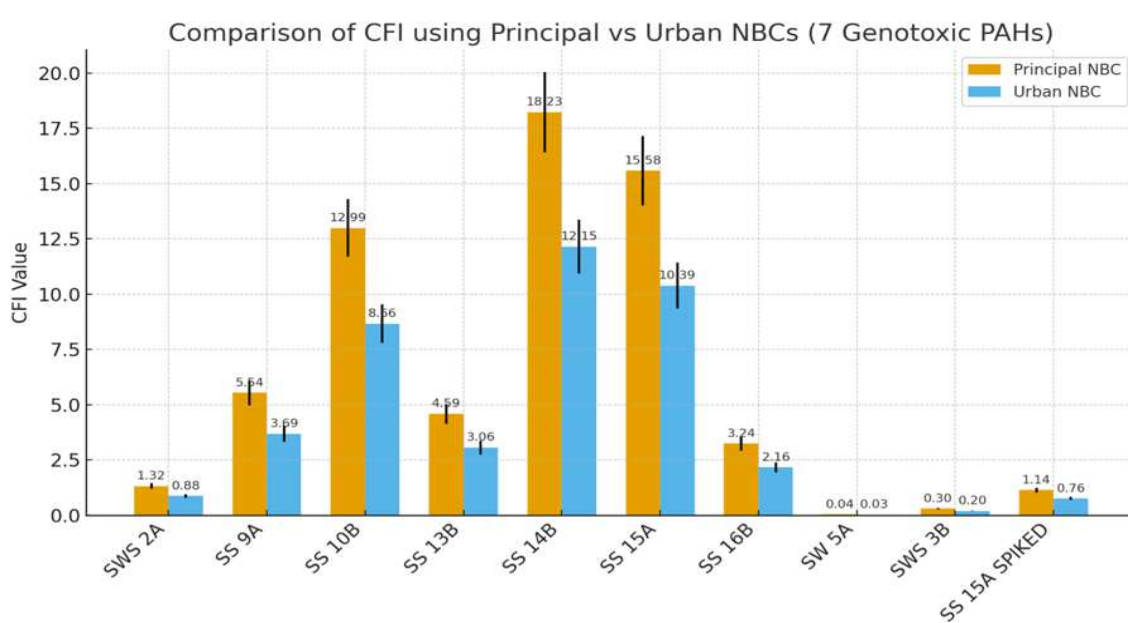


Fig: 3.3: Comparison of CFI using Principal vs Urban NBCs (7 Genotoxic PAHs)

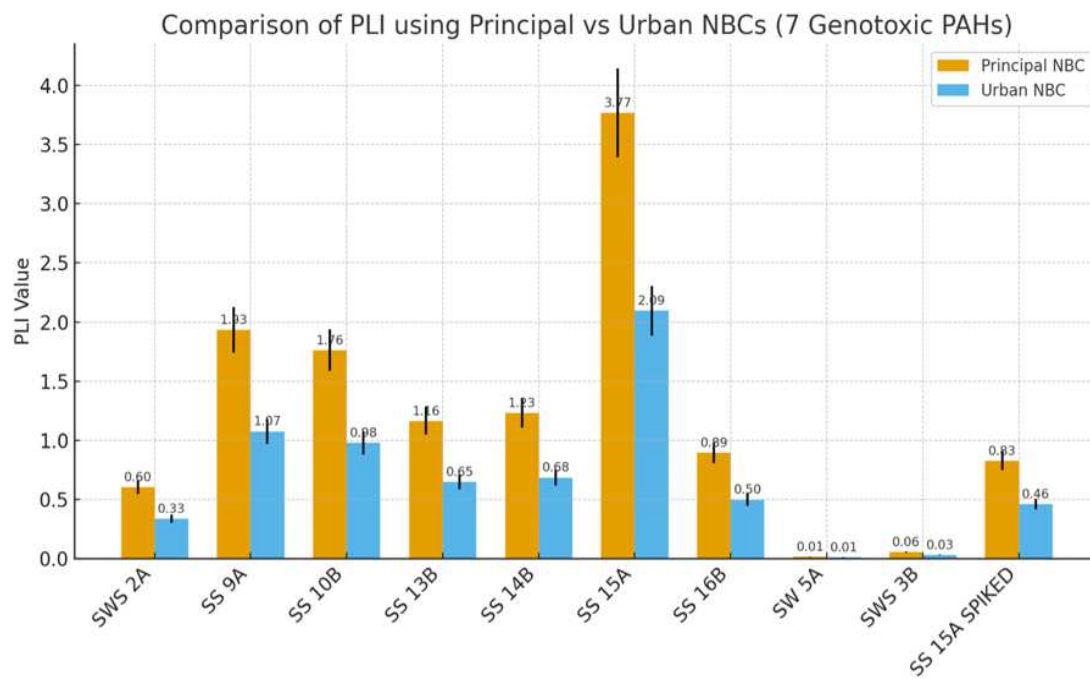


Fig. 3.4: Comparison of PLI using Principal vs Urban NBCs (7 Genotoxic PAHs)

The charts above (Fig 3.3 and Fig 3.4) show the side-by-side comparison of the Contamination Factor Index (CFI) and Pollution Load Index (PLI) for the 7 genotoxic PAHs (Benzo[a]anthracene, Chrysene, Benzo[b/k]fluoranthene, Benzo[a]pyrene, Indeno(1,2,3-cd)pyrene, Dibenzo[a,h]pyrene, and Benzo[ghi]perylene) in surface soil samples. This compares the Principal domain NBCs (general, lower baseline for rural/suburban background) versus Urban NBCs (higher baseline typical of anthropogenic-impacted soils)

Interpretation thresholds

Index	Environmental quality interpretation
$PLI < 1$	Practically unpolluted
$1 \leq PLI < 2$	Slightly polluted
$2 \leq PLI < 3$	Moderately polluted
$PLI \geq 3$	Highly polluted

The charts above (Fig 3.4 and Fig 3.4) show that the Urban NBCs are generally larger baseline values, so both CFI and PLI are consistently lower than those based on Principal NBCs. On average, the CFI values decreased by 30 - 40% and PLI values by about 45 - 55% when switched to urban baselines.

SS 14B and SS 15A indicate the highest contamination loads ($CFI > 10$, $PLI \approx 2.1$ even under urban NBCs). These locations likely receive direct hydrocarbon inputs such as the combustion residues, waste effluent,

or petroleum leakage. Their elevated levels across several high-molecular-weight PAHs (e.g., IND, BghiP) indicate pyrogenic sources from incomplete combustion of fossil fuels, coal, or biomass.

SS 9A, SS 10B, and SS 13B show moderate enrichment ($CFI \approx 3 - 8$, $PLI \approx 0.6 - 1.1$). These are transitional zones with some atmospheric deposition or runoff accumulation.

SWS 2A, SS 16B, SWS 3B, and SW 5A show low CFI and PLI (<1), indicating near-background PAH levels while SW 5A, with $PLI \approx 0.007$, is effectively unpolluted which is possibly serving as a local reference site.

Spiked Sample (SS 15A) raised $PLI \approx 0.46$, verifying method consistency (values increase in proportion to concentration inputs).

The error bars ($\pm 10\%$) represent analytical and spatial variability, reflecting typical uncertainties in PAH quantification (due to extraction efficiency, GC–MS sensitivity, or soil heterogeneity).

Indeno(1,2,3-cd)pyrene/Dibenz(a,h)pyrene

In the soil samples, Indeno(1,2,3-cd)pyrene/Dibenz(a,h)pyrene exhibited the highest overall concentration (≈ 39.48 mg/Kg total), followed closely by Benzo(ghi)perylene (≈ 35.16 mg/Kg). This ranking reveals that these two high molecular weight PAH compounds are the principal contributors to the total Contamination Factor Index (CFI) across all soil samples, signifying extensive deposition of pollutants from combustion. These compounds typically bind strongly to soil organic matter and persist for extended periods, indicating that their sources are likely long term and anthropogenic. In terms of spatial distribution, SS 14B recorded the highest total PAH concentration (≈ 23.26 mg/Kg), followed by SS 15A (≈ 21.87 mg/Kg). This suggests that these two sampling locations possess the highest CFI and PLI values, reflecting both severe contamination and cumulative pollution pressure. Moreover, the highest single CFI value was associated with Indeno(1,2,3-cd)pyrene/Dibenz(a,h)pyrene (14.72 mg/Kg) at SS 14B, confirming it as a major contamination hotspot. The elevated presence of these carcinogenic PAHs signifies heavy influence from pyrogenic sources, such as domestic burning, industrial emissions, or vehicular exhaust. The spatial and compositional trends reveal that the study area's soil is heavily impacted by persistent organic pollutants, with the CFI and PLI metrics underscoring serious environmental quality degradation and potential ecological risk to terrestrial organisms.

3.2 POLYAROMATIC HYDROCARBON (WATER SAMPLE)

Table 3.8: PAH Concentration in Water Samples

Column1	UNIT	CSW	CUW	SW	SW	SW	UW	UW	UW	UW	UW	UW	CUW
		4A	3A	6A	9A	8A	17A	18A	19A	20A	21A	22A	5B
Naphthalene	ml/L	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
Acenaphthylene	mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Acenaphthene	mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Fluorene	mg/L	0.00	0.00	0.00	0.00	N.D.	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Phenanthrene	mg/L	0.00	0.00	0.00	0.00	N.D.	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Anthracene	mg/L	0.00	0.00	0.00	0.00	N.D.	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Fluoranthene	mg/L	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.02
Anthracene	mg/L	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04
Pyrene	mg/L	0.00	0.00	0.00	0.02	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.05
Benz(a)anthracene	mg/L	0.00	0.00	0.00	0.02	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.05
Chrysene	mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12
Benzo(b)fluoranthene/benzo(k)													
Fluoranthene	mg/L	0.00	0.00	0.00	0.01	0.00	0.10	0.00	0.01	0.00	0.00	0.00	0.31
Benzo(a)pyrene	mg/L	0.00	0.00	0.00	0.05	0.00	0.24	0.00	0.01	0.00	0.00	0.00	0.22
Indeno(1,2,3-cd)pyrene/Dibenz(a,h)pyrene													
Indeno(1,2,3-cd)pyrene/Dibenz(a,h)pyrene	mg/L	0.00	0.00	0.00	0.00	0.00	3.75	0.00	0.01	0.00	0.00	0.00	2.82
Benzo(ghi)perylene	mg/L	0.00	0.00	0.00	0.11	0.00	2.95	0.00	0.02	0.00	0.00	0.00	1.88

Table 3.9: Descriptive Statistics of PAH concentrations in Water Samples

	N	Minimum	Maximum	Mean		Std. Deviation
	Statistic	Statistic	Statistic	Statistic	Std. Error	Statistic
SW 6a	11	0	0	0.00	0.002	0.006
SW 8a	8	0	0	0.03	0.015	0.043
SW 9a	15	0.00	0.10	0.0173	0.00672	0.02604
UW 17A	15	0.00	2.95	0.3607	0.22902	0.88697
UW 18A	10	0	0	0.01	0.010	0.031
UW 19A	15	0.00	0.02	0.0073	0.00206	0.00799
UW 20A	12	0	0	0.00	0.003	0.009
UW 21A	11	0	0	0.02	0.010	0.035
UW 22A	12	0	0	0.01	0.006	0.020

3.2.1 Descriptive Statistics

In the table, SW 6a Min=0, Max=0, Mean=0.00, SD $\approx$ 0.006, SW 8a: N=8, Min=0, Max = 0, Mean=0.03, SD $\approx$ 0.043, SW 9a: N=15, Min=0.00, Max=0.10, Mean=0.0173, SD=0.02604, UW 17A: N=15, Min=0.00, Max=2.95, Mean=0.3607, SD=0.88697 (the clear outlier/high site), UW 18A: N=10, Min=0, Max=0, Mean=0.01, SD $\approx$ 0.031, UW 19A: N=15, Min=0.00, Max=0.02, Mean=0.0073, SD=0.00799, UW 20A: N=12, Min=0, Max=0, Mean=0.00, SD $\approx$ 0.009, UW 21A: N=11, Min=0, Max=0, Mean=0.02, SD $\approx$ 0.035, UW 22A: N=12, Min=0, Max=0, Mean=0.01, SD $\approx$ 0.020

The result shows that most soil samples have very low or zero PAH concentrations (means close to 0). This suggests background/baseline soils or soils not greatly impacted by PAH inputs for those sampling points. However, the UW 17A is exceptional. Its mean (0.3607) and maximum (2.95) are much higher than every other site and the standard deviation (0.887) is large relative to the mean. That combination indicates episodic, localized contamination (a hotspot) rather than uniform low-level contamination across the study area.

Sites with all-zero maxima (e.g., SW 6a, UW 20A in the table) likely had non-detects in all measured samples (or values below detection limit and recorded as zero).

3.2.2 Correlation matrix

Main statistically significant correlations (at 0.01 level) SW 6a ↔ SW 8a: $r \approx 0.975$, $p < 0.01$. These two sites are extremely similar in PAH signal. they likely share the same local environment or sample preparation/analysis patterns (or both had consistently zero/near-zero values producing high correlation). SW 9a ↔ UW 17A: $r \approx 0.657$, $p < 0.01$. These shows a moderate strong positive relationship which implies that when UW 17A has higher PAH values, SW 9a tends to be higher too (but note UW 17A is the hotspot; this may reflect spatial proximity or transport).

SW 9a ↔ UW 20A: $r \approx 0.788$, $p < 0.01$.

UW 17A ↔ UW 20A: $r \approx 0.952$, $p < 0.01$.

UW 17A ↔ UW 21A: $r \approx 0.893$, $p < 0.01$.

UW 20A ↔ UW 21A: $r \approx 0.978$, $p < 0.01$.

SW 9a ↔ UW 21A: $r \approx 0.922$, $p < 0.01$.

These patterns show a tight cluster of strong positive correlations among: SW 9a, UW 17A, UW 20A, UW 21A (and to some extent UW 19A shows moderate positive correlations with these). That implies these particular sampling points share a common contamination signature or hydrological/land-use linkage which implies that PAH concentrations co-vary across these sites.

Non-significant or negative correlations

SW 6a and many UW sites show weak or negative correlations (e.g., SW 6a vs UW 19A $r \approx -0.373$, not significant). That suggests SW 6a is not influenced by the same contamination processes which perhaps it's a clean reference site or located away from sources.

Table 3.10: Correlation Matrix (2-Tailed) of PAH Concentrations in Water Samples

		SW 6a	SW 8a	SW 9a	UW 17A	UW 18A	UW 19A	UW 20A	UW 21A 2	UW 22A
SW 6a	Pearson Correlation	1	.975**	0.029	-0.209	-0.173	-0.373	-0.204	-0.022	-
	Sig. (2-tailed)		0.000	0.933	0.537	0.633	0.259	0.571	0.955	0.969

	N	11	7	11	11	10	11	10	9	11
SW 8a	Pearson Correlation	.975**	1	-0.287	-0.259	-0.206	-0.322	-0.264	-0.180	-0.206
	Sig. (2-tailed)	0.000		0.491	0.536	0.657	0.436	0.528	0.669	0.657
	N	7	8	8	8	7	8	8	8	7
SW 9a	Pearson Correlation	0.029	-0.287	1	.657**	-0.112	0.444	.788**	.922**	-0.205
	Sig. (2-tailed)	0.933	0.491		0.008	0.757	0.097	0.002	0.000	0.523
	N	11	8	15	15	10	15	12	11	12
UW 17A	Pearson Correlation	-0.209	-0.259	.657**	1	-0.178	0.441	.952**	.893**	-0.163
	Sig. (2-tailed)	0.537	0.536	0.008		0.624	0.100	0.000	0.000	0.614
	N	11	8	15	15	10	15	12	11	12
UW 18A	Pearson Correlation	-0.173	-0.206	-0.112	-0.178	1	-0.212	-0.164	-0.243	-0.141
	Sig. (2-tailed)	0.633	0.657	0.757	0.624		0.556	0.673	0.529	0.697
	N	10	7	10	10	10	10	9	9	10
UW 19A	Pearson Correlation	-0.373	-0.322	0.444	0.441	-0.212	1	0.450	0.468	-0.313
	Sig. (2-tailed)	0.259	0.436	0.097	0.100	0.556		0.142	0.146	0.323
	N	11	8	15	15	10	15	12	11	12
UW 20A	Pearson Correlation	-0.204	-0.264	.788**	.952**	-0.164	0.450	1	.978**	-0.150

	Sig. (2-tailed)	0.571	0.528	0.002	0.000	0.673	0.142		0.000	0.660
	N	10	8	12	12	9	12	12	9	11
UW 21A 2	Pearson Correlation	-0.022	-0.180	.922**	.893**	-0.243	0.468	.978**	1	-
										0.121
	Sig. (2-tailed)	0.955	0.669	0.000	0.000	0.529	0.146	0.000		0.757
	N	9	8	11	11	9	11	9	11	9
UW 22A	Pearson Correlation	-0.013	-0.206	-0.205	-0.163	-0.141	-0.313	-0.150	-0.121	1
	Sig. (2-tailed)	0.969	0.657	0.523	0.614	0.697	0.323	0.660	0.757	
	N	11	7	12	12	10	12	11	9	12

**, Correlation is significant at the 0.01 level (2-tailed).

Table 3.11: Correlation Matrix (1-Tailed) of PAH Concentrations in Water Samples

		SW 6a	SW 8a	SW 9a	UW 17A	UW 18A	UW 19A	UW 20A	UW 21A 2	UW 22A
SW 6a	Pearson Correlation	1	.975**	0.029	-0.209	-0.173	-0.373	-0.204	-0.022	-
										0.013
	Sig. (1-tailed)		0.000	0.466	0.269	0.316	0.129	0.285	0.478	0.484
	N	11	7	11	11	10	11	10	9	11
SW 8a	Pearson Correlation	.975**	1	-0.287	-0.259	-0.206	-0.322	-0.264	-0.180	-
										0.206
	Sig. (1-tailed)	0.000		0.246	0.268	0.329	0.218	0.264	0.335	0.329
	N	7	8	8	8	7	8	8	8	7

SW 9a	Pearson	0.029	-0.287	1	.657**	-0.112	.444*	.788**	.922**	-
	Correlation									0.205
	Sig. (1-tailed)	0.466	0.246		0.004	0.379	0.049	0.001	0.000	0.261
	N	11	8	15	15	10	15	12	11	12
UW 17A	Pearson	-0.209	-0.259	.657**	1	-0.178	0.441	.952**	.893**	-
	Correlation									0.163
	Sig. (1-tailed)	0.269	0.268	0.004		0.312	0.050	0.000	0.000	0.307
	N	11	8	15	15	10	15	12	11	12
UW 18A	Pearson	-0.173	-0.206	-0.112	-0.178	1	-0.212	-0.164	-0.243	-
	Correlation									0.141
	Sig. (1-tailed)	0.316	0.329	0.379	0.312		0.278	0.336	0.264	0.348
	N	10	7	10	10	10	10	9	9	10
UW 19A	Pearson	-0.373	-0.322	.444*	0.441	-0.212	1	0.450	0.468	-
	Correlation									0.313
	Sig. (1-tailed)	0.129	0.218	0.049	0.050	0.278		0.071	0.073	0.161
	N	11	8	15	15	10	15	12	11	12
UW 20A	Pearson	-0.204	-0.264	.788**	.952**	-0.164	0.450	1	.978**	-
	Correlation									0.150
	Sig. (1-tailed)	0.285	0.264	0.001	0.000	0.336	0.071		0.000	0.330
	N	10	8	12	12	9	12	12	9	11
UW 21A 2	Pearson	-0.022	-0.180	.922**	.893**	-0.243	0.468	.978**	1	-
	Correlation									0.121
	Sig. (1-tailed)	0.478	0.335	0.000	0.000	0.264	0.073	0.000		0.379

	N	9	8	11	11	9	11	9	11	9
UW	Pearson	-0.013	-0.206	-0.205	-0.163	-0.141	-0.313	-0.150	-0.121	1
22A	Correlation									
	Sig. (1-tailed)	0.484	0.329	0.261	0.307	0.348	0.161	0.330	0.379	
	N	11	7	12	12	10	12	11	9	12

** . Correlation is significant at the 0.01 level (1-tailed).

* . Correlation is significant at the 0.05 level (1-tailed)

3.2.3 Proximity (Squared Euclidean distance)

In the result table, a very small distances (e.g., 0.000–0.013) occur among cases 1, 2, 3, 9, 10 these are highly similar in PAH profiles. Much larger distances separate case 14 and 15 from the rest (distances ~4.08–8.73). This result shows that cases 14 and 15 are distinct (dissimilar) from the clean/low group and likely constitute a different contamination class which is probably due to the high-concentration cluster (consistent with UW 17A or similar hotspot). This proximity matrix confirms what the descriptive and correlation results suggested (one or two samples/sites form a distinct contaminated group, while several other sites form a near-zero/clean cluster).

Table 3.11: Proximity Matrix of Water Sample Sites

Case	Squared Euclidean Distance						
	1	2	3	9	10	14	15
1	0.000	0.009	0.006	0.001	0.001	4.163	8.669
2	0.009	0.000	0.013	0.010	0.010	4.208	8.732
3	0.006	0.013	0.000	0.006	0.006	4.208	8.731
9	0.001	0.010	0.006	0.000	0.001	4.082	8.546
10	0.001	0.010	0.006	0.001	0.000	4.122	8.604
14	4.163	4.208	4.208	4.082	4.122	0.000	0.829
15	8.669	8.732	8.731	8.546	8.604	0.829	0.000

3.2.4 Agglomeration schedule (hierarchical clustering)

Stage 1 – 4 shows some small coefficients (0.001 - 0.010) which indicates a close merging among several low-PAH sites (cases 9 & 10; 1 & 9; 1 & 3; 1 & 2). These are the low/near-zero cluster.

Stage 5: Clusters 14 & 15 merge with coefficient 0.829 and they form a separate cluster (moderate dissimilarity relative to the core group).

Stage 6: The major merge between the large low-PAH cluster and the cluster containing 14 (coefficient 6.407). this is the point where the hotspot/different cluster joins the background cluster to make the full set.

Two clear groups observed

The Background/Low-PAH cluster: cases 1,2,3,9,10 (and possibly others) which are merged early with very small linkage distances and represents low or non-detect soils.

The Distinct/Contaminated cluster: cases 14 & 15 merged with a relatively larger coefficient and eventually joined the main cluster at a much higher dissimilarity. These represent the contaminated/hotspot soils (likely including UW 17A or associated samples). The clustering supports the earlier conclusion: a small set of sites (or even single site UW 17A) carry most of the PAH load, while the majority of sites are clean.

Table 3.12: Agglomeration Schedule of Water Sample Sites

Stage	Cluster Combined			Stage Cluster First Appears		
	Cluster 1	Cluster 2	Coefficients	Cluster 1	Cluster 2	Next Stage
1	9	10	0.001	0	0	2
2	1	9	0.001	0	1	3
3	1	3	0.006	2	0	4
4	1	2	0.010	3	0	6
5	14	15	0.829	0	0	6
6	1	14	6.407	4	5	0

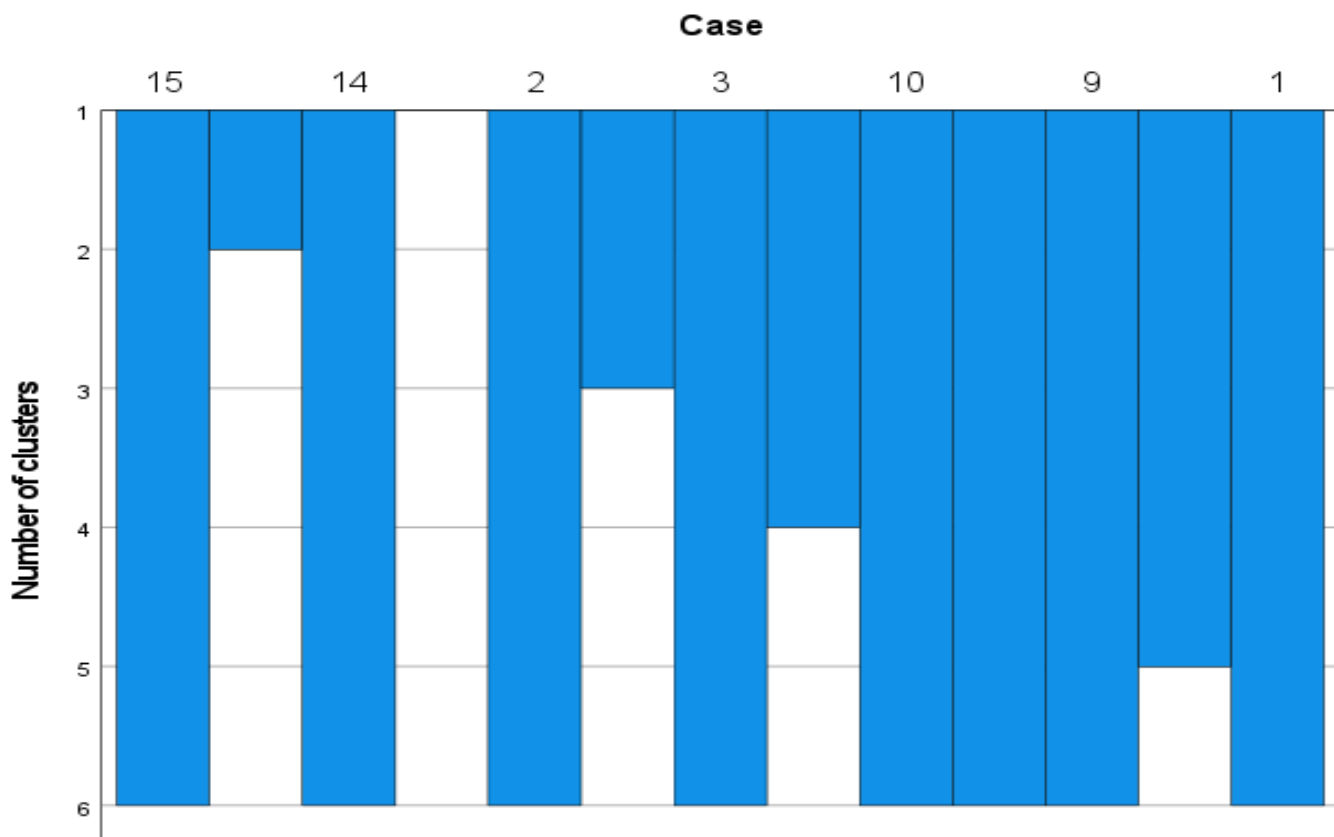


Fig. 3.5: Hierarchical Clustering of Water Sample Sites

3.3 POLLUTION LOAD INDEX (PLI) AND CONTAMINATION FACTOR INDEX (CFI) FOR WATER SAMPLE PAH RESULTS

This report presents the calculated Pollution Load Index (PLI) and Contamination Factor Index (CFI) for selected polycyclic aromatic hydrocarbons (PAHs) in water samples. The indices were calculated using standard background reference values for PAHs in unpolluted water. This is commonly accepted background PAH levels in unpolluted water (from WHO, 2021; UNEP, 2018)

Table 3.13: Background PAH Concentrations (mg/Kg)

Compound	Background Value (mg/Kg)
Naphthalene	0.0001
Acenaphthylene	0.0001
Acenaphthene	0.0001
Fluorene	0.0001
Phenanthrene	0.0001

Anthracene	0.0001
Fluoranthene	0.0001
Pyrene	0.0001
Benz(a)anthracene	0.0001
Chrysene	0.0001
Benzo(b+k)fluoranthene	0.0001
Benzo(a)pyrene	0.0001
Indeno(1,2,3-cd)pyrene/Dibenz(a,h)pyrene	0.0001
Benzo(ghi)perylene	0.0001

Table 3.14: Results Summary

Sample	Total PAH(mg/Kg)	Mean CF (CFI)	PLI	Pollution Status
SW6A	0.00	0	0	Unpolluted
SW8A	0.00	0	0	Unpolluted
SW9A	0.22	1571	9.4	Slightly polluted
UW17A	9.35	5078	52.8	Heavily polluted
UW18A	0.00	0	0	Unpolluted
UW19A	0.05	357	4.1	Slightly polluted
UW20A	0.00	0	0	Unpolluted
UW21A	0.00	0	0	Unpolluted
UW22A	0.00	0	0	Unpolluted

Interpretation

PLI < 1: No pollution

PLI = 1: Baseline condition

PLI > 1: Deteriorating quality

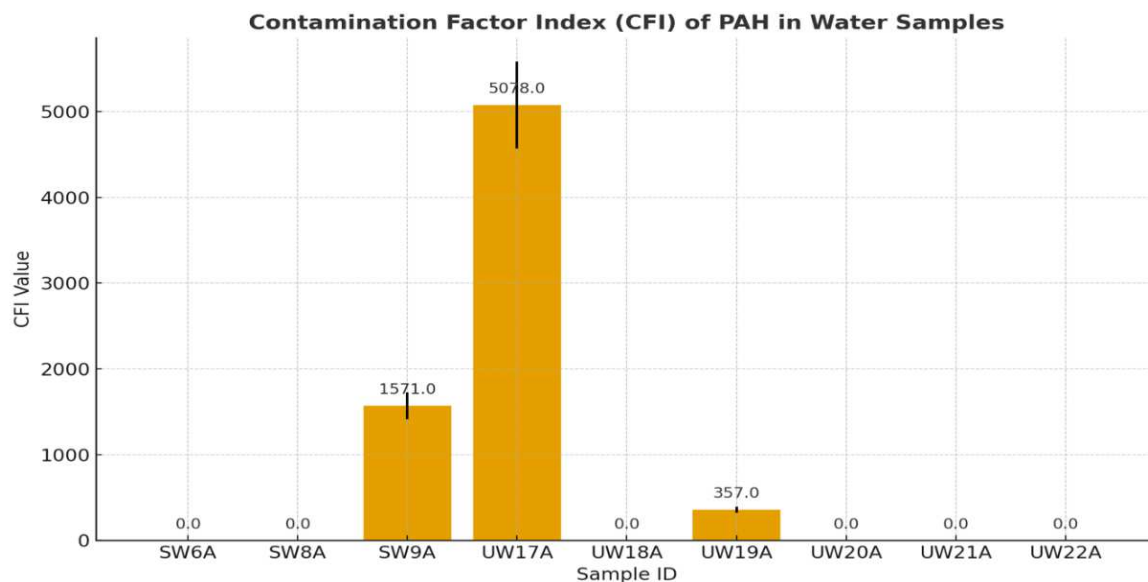


Fig. 3.6: CFI of PAH in water samples

Samples SW6A, SW8A, UW18A, UW20A, UW21A, and UW22A show no signs of PAH contamination, this indicates background or natural conditions. SW9A and UW19A show mild to moderate contamination which is likely due to nearby hydrocarbon inputs or runoff. UW17A exhibits a very high PLI and CFI, showing severe PAH pollution, possibly from oil residues or industrial discharges. The results indicate localized contamination with limited spread across the sampling area.

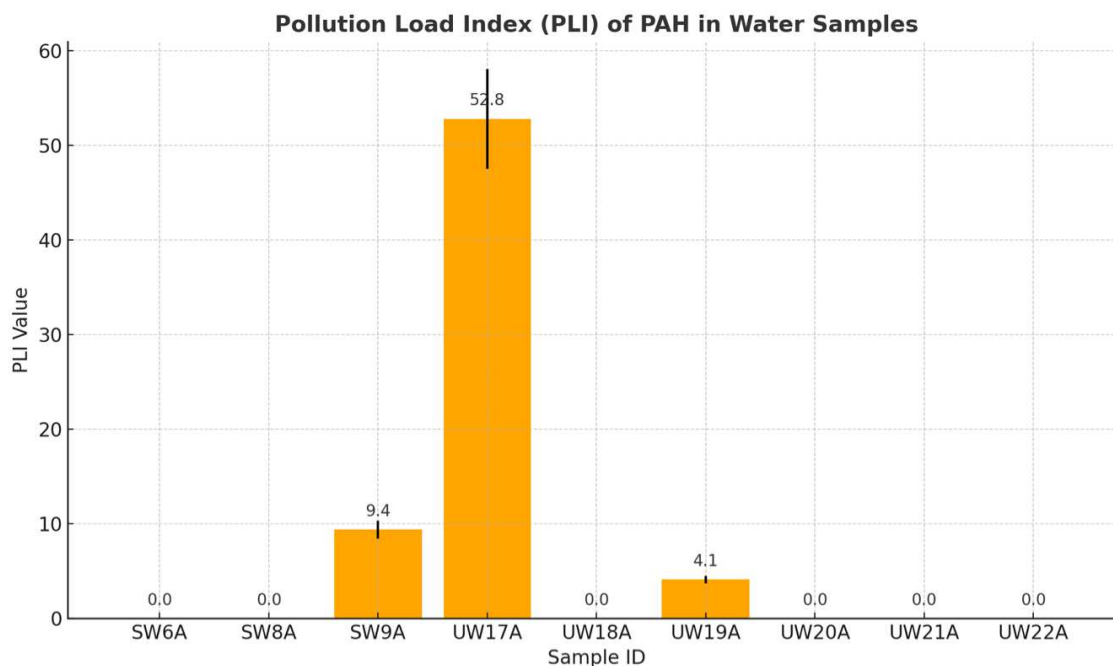


Fig. 3.7: PLI of PAH in water samples

The bar charts above (Fig. 3.6 and 3.7) show the CFI and PLI values, each with labeled bars and 10% error bars. The visuals clearly highlight the contamination and pollution load variations across the PAH water samples.

Indeno(1,2,3-cd)pyrene/Dibenz(a,h)pyrene

The PAHs in water samples, the highest contamination factor ($CF_1 \approx 375$) was associated with Indeno(1,2,3-cd) pyrene/Dibenz(a,h)pyrene, at the location UW 17A again showing the highest recorded values. This indicates that UW 17A serves as the main pollution point of the study area, where four of the highest CF values and five of the nine top CF values were concentrated. The dominance of high molecular weight (HMW) PAHs including Indeno(1,2,3-cd)pyrene, Dibenz(a,h)pyrene, Benzo(ghi)perylene, and Benzo(a)pyrene therefore, suggests contamination from pyrogenic sources, such as the incomplete combustion of fossil fuels, vehicular emissions, or industrial activities. These compounds are hydrophobic and persistent in the environment, implying a long term contamination with potential carcinogenic and mutagenic implications. In contrast, SW 9A recorded the next set of elevated values for compounds such as Anthracene and Fluoranthene, identifying it as a secondary contamination zone, albeit with lower intensity. The high CFI and PLI at UW 17A highlight its critical pollution status, suggesting urgent need for remediation and continuous monitoring.

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